Pergamon

Tetrahedron Letters, Vol. 36, No. 9, pp. 1539-1540, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(95)00082-8

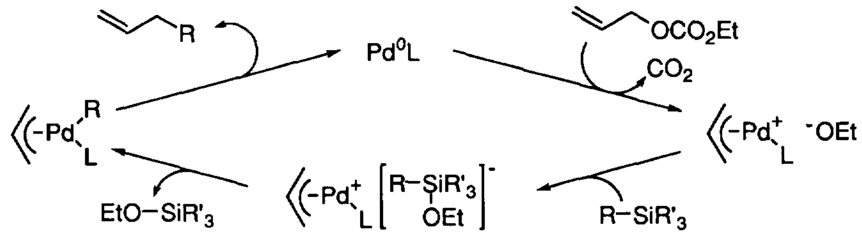
Palladium-Catalyzed Cross-Coupling of Allylic Carbonates with Alkenylfluorosilanes in the Absence of Fluoride Ion

Hayao Matsuhashi, Yasuo Hatanaka,† Manabu Kuroboshi, and Tamejiro Hiyama*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226, Japan
†Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229, Japan

Abstract: Alkenylfluorosilanes smoothly underwent cross-coupling reaction with allylic carbonates in the presence of a palladium catalyst and *in the absence of fluoride ion* to give 1,4-dienes in good yields with retention of configuration.

Organo(fluoro)silanes have been shown to undergo palladium-catalyzed cross-coupling reaction with organic electrophiles with the aid of 1 (or sometimes more) equivalent(s) of fluoride ion.[1] Fluoride ion which is needed to activate the organo(fluoro)silane to produce a pentacoordinated silicate may cleave silyl protecting groups and induce various base-promoted side reactions. We have been looking for a solution for this problem and focused on a π-allylpalladium alkoxide intermediate, which should be produced from a palladium(0) complex and an allylic carbonate.[2] We assumed, if the co-generated alkoxide ion can activate an organosilane by giving rise to a pentacoordinated silicate,[3] palladium-catalyzed cross-coupling of allylic carbonates with organosilanes should be achieved *under neutral conditions in the absence of fluoride ion* (Scheme 1).[4] In this letter, we report our hypothesis really worked well so that various allylic carbonates could couple with alkenylfluorosilanes to give 1,4-dienes.[5]

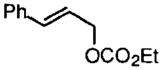
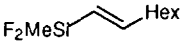
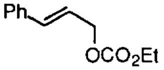
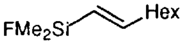
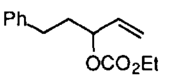
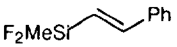
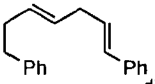
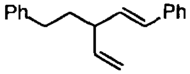
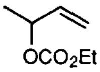
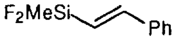
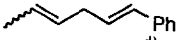
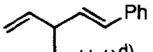
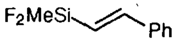
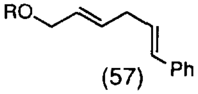
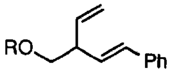


Scheme 1

Preliminary experiments showed that the reaction was quite sensitive to a palladium catalyst and a phosphine ligand.[6] After optimization of the catalytic system, the desired reaction was easily realized using $Pd(OAc)_2$ (5 mol%) and PPh_3 (5 mol%) in DMF at 60 °C. Alkenyldifluorosilanes reacted with various allyllic carbonates under the standard conditions to give 1,4-dienes (Table 1). Alkenyl(difluoro)methylsilanes and alkenyl(fluoro)dimethylsilanes exhibited comparable reactivity (runs 1 and 2). (*E*)-Cinnamyl ethyl carbonate as the substrate gave α-substitution product only (run 1), but 1- or 3- substituted carbonates (runs 3 to 6) gave 2 : 1 to 4.6 : 1 mixtures of α and γ-coupled products. The coupling occurred in these cases at a less substituted position predominantly. Run 6 shows clearly that the silyl protecting group tolerates the reaction conditions to give coupled products in 69% yield. Vinyltrimethylsilane was inactive to recover the carbonate substrate.

Based on our previous findings, we may suggest that the present reaction proceeds via transmetalation through a pentacoordinated silicate species produced from an alkenylfluorosilane and a π-allyl palladium alkoxide complex (Scheme 1).[1] We are studying further mechanistic details.[7]

Table 1 Cross-Coupling of allyl carbonates with alkenylsilanes[a)]

run	allylic carbonates	organosilanes	time/h	product(s) (yield/%)[b)]
1			28	 (73)
2			18	 (78)[c)]
3			1	 (70)[d)]  (20)[d)]
4			1.5	 (62)[d)]  (14)[d)]
				 
5	R = Bn		1.5	(57) (23)
6	R = *t*-BuMe2Si		4	(46) (23)

a) Standard conditions: A mixture of Pd(OAc)$_2$ (0.025 mmol) and PPh$_3$ (0.025 mmol) in DMF (1 ml) was stirred at room temperature for 5 min in a sealed tube. Then an allylic carbonate (0.50 mmol) and an alkenylfluorosilane (1.0 or 1.5 mmol) were added to the reaction mixture, and the whole mixture was stirred at 60 °C until all of the carbonate was consumed. b) Isolated yields are given. c) Dimerization product 1,4-diphenyl-1,5-hexadiene was coproduced in 12% yield. d) The selectivity was determined by ^{1}H NMR.

References and Notes

1. Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845. Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471 and references cited therein.
2. Tsuji, J.; Shimizu, I.; Minami, I.; Ohhashi, Y.; Sugiura, T., Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523.
3. Cross-coupling of organoalkoxysilane mediated by fluoride ion may proceed through a similar intermediate. Tamao, K.; Kobayashi, K.; Ito, Y. *Tetrahedron Lett.* **1989**, *30*, 6051.
4. Palladium catalyzed cyanation with trimethylsilylcyanide need no activator. Tsuji, Y.; Yamada, N.; Tanaka, S. *J. Org. Chem.* **1993**, *58*, 16.
5. Other examples of the reaction of alkenylmetal with allylic compounds: Valle, L. D.; Stille, J. K.; Hegedus, L. S. *J. Org. Chem.* **1990**, *55*, 3019. Boden, C.; Pattenden, G. *Synlett* **1994**, 181. Miyaura, N.; Yano, T.; Suzuki, A. *Tetrahedron Lett.* **1980**, *21*, 2865. Kobayashi, Y.; Ikeda, E. *J. Chem. Soc., Chem. Commun.* **1994**, 1789. Agrios, K. A.; Srebnik, M. *J. Org. Chem.* **1994**, *59*, 5468. Matsushita, H.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 2882.
6. For example, the reaction carried out with Pd : PPh$_3$ = 1 : 2 gave cinnamyl ethyl ether in 54%. In the absence of phosphine ligand, the reaction did not take place. Details will be reported in elsewhere.
7. The present work was partially supported by Grant-in-Aid from Ciba-Geigy Foundation (Japan) for the Promotion of Science.

(*Received in Japan* 12 *December* 1994; *accepted* 27 *December* 1994)